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PROPELLANTS FOR GAS GENERATORS

The present invention relates to solid propellants for gas generators (gas-generating mixtures), wherein said propellants are mainly intended for use in propelling charges for gas generators used in airbags or seat-belt pre-tensioning devices on the basis of nitrogen-rich fuels having a carbon content as low as possible. The solid propellants for gas generators further include an essentially chemically-inert slag trap in highly dispersed form which has a high fusion point, wherein said slag trap acts as an inner filter and substantially prevents the formation of powder (dust-type) particles as well as their exit from the housing of the gas generator.

Thus, the present invention relates to a process for trapping the liquid and solid burn-up products and dust-type slag particles, respectively, within the propelling charge for gas generators directly during the formation. It is thus possible to use a simple structured filter package within the housing of the gas generator.

The present invention further relates to the use of catalysts on the basis of platinum metals (Ru, Os, Rh, Ir, Pd, Pt) or metal alloys of platinum metals or copper on the slag traps as carriers in solid propellants for gas generators. In particular, it relates to the use in solid propelling charges for gas generators used in airbags.

An airbag essentially comprises a housing of the gas generator filled with the propelling charges for gas generators, generally in tablet form, and an initial detonator (squib) for detonating the propelling charge for gas generators, and also a gas bag. Suitable detonators are disclosed, for example, in US 4,931,111. The gas bag, which is initially folded into a small bag, is filled, after the initial detonation, with the gases produced in the burn-up of the propelling charge for gas generators and reaches its full volume in a time period of about 10-50 ms. The exit of hot sparks, molten material and solids from the gas generator into the gas bag has to be largely prevented, since it could result in the destruction of the gas bag or in injury to the vehicle passengers. This is achieved by binding and filtering of the slag formed by burning up the propelling charge for gas generators.

Propelling charges for gas generators to be used in airbags on the basis of sodium azide are well known. However, the use of the highly toxic sodium azide requires a work intensive and costly process for the preparation of the propelling charges for gas generators. Furthermore, the worldwide ever increasing number of non-burned-up propelling charges for gas generators in used vehicles leads to a disposal and security problem.

Therefore, in recent years there have been efforts to find suitable substitutes for sodium azide.

DE-A-44 35 790 discloses propellants for gas generators on the basis of guanidine compounds on suitable carriers, which essentially exhibit an improved burn-up behaviour and an improved building of the slag. DE-A-44 35 790 does not give any hints as to the use of essentially chemically-inert slag traps in highly dispersed form which have a high fusion point

or to the use of catalysts in propelling charges for gas generators.

From EP-B-0 482 852 and the prior art referred to in this document azide-free propelling charges for gas generators, in particular for use in airbags, are known. The gas-generating mixture disclosed in EP-B-0 482 852 contains a) a fuel selected from aminotetrazole, tetrazole, bitetrazole and metal salts thereof and triazole compounds and metal salts thereof; b) an oxygen containing oxidizing agent selected from nitrates and perchlorates of alkaline metals, alkaline earth metals, lanthanides and ammonium, and chlorates and peroxides of alkaline metals and alkaline earth metals; and either c) a high temperature slag forming material selected from alkaline earth metal oxides, -hydroxides, -carbonates, -oxalates, -peroxides, -nitrates, -chlorates and -perchlorates and alkaline earth metal salts of tetrazoles, bitetrazoles and triazoles, and d) a low temperature slag forming material selected from silicon dioxide, boron oxide, vanadium pentoxide, naturally occurring clays and talcum, alkali metal silicates, -borates, -carbonates, -nitrates, -perchlorates and -chlorates and alkali metal salts of tetrazoles, bitetrazoles and triazoles; or e) a high temperature slag forming material selected from transition metal oxides, -hydroxides, -carbonates, -oxalates, -peroxides, -nitrates, -chlorates and -perchlorates; and f) a low temperature slag forming material which is silicon dioxide, wherein the amount of d) or f) is sufficient to achieve the formation of a coherent mass or slag, however, is not large enough to build a liquid with low viscosity. It is evident that a single material can be used in more than one category.

The essential advantage of a propelling charge for gas generators of this kind is the advantageous formation of a slag

which can be easily filtered from the formed gaseous burn-up products. A further advantage is the high gas yield.

However, disadvantages of this kind of propelling charges for gas generators are as follows:

With respect to the provision of a propelling charge for gas generators with a most advantageous slag formation compromises had to be made with respect to the burn-up behaviour (burn-up rate), the gas formation, the properties with respect to the preparation of the pellets and other processing factors and, in particular, with respect to the quality of the gas, i.e. with respect to the portion of toxic gaseous burn-up products. Furthermore, the number of suitable fuels is relatively limited.

EP-B-0 482 852 does not give any hints as to how these problems can be solved by modifying the composition of the propelling charge for gas generators.

In US 4,948,439, the same inventor refers to the problems with respect to the formation of toxic gaseous burn-up products when using azide-substitutes, such as tetrazole compounds (e.g. aminotetrazole and metal salts thereof) and mixtures thereof in propelling charges for gas generators.

However, the teaching of US 4,948,439 does not provide any suggestion as to how the portion of toxic gaseous burn-up products developed during the burning up of propelling charges for gas generators which contain as fuel tetrazole or triazole compounds, metal salts or mixtures thereof, can be reduced. On the contrary, a process for inflating an airbag is described according to which a primary gas mixture is initially obtained by ignition of a propelling charge for gas generators which contains as a fuel at least one tetrazole or

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trizole compound. The primary gas mixture is then diluted by mixing with surrounding atmosphere to such a degree that the content of toxic gaseous burn-up products from the primary gas mixture is reduced to a toxicologically acceptable amount.

However, the mixing with the surrounding atmosphere leads to a more complex total airbag system (size, structure, etc.). A problem is the rate with which the airbag has to be inflated (10-50 ms) in case that in addition surrounding atmosphere has to be drawn in.

DE-C-44 01 213 discloses gas-generating mixtures comprising a fuel, an oxidizing agent, a "catalyst" and a cooling agent, characterized in that the oxidizing agent is $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ and the catalyst is a metal oxide or a mixture of metal oxides or a metal mixed oxide.

In addition, DE-C-44 01 214 discloses gas-generating mixtures having a similar composition, in which the catalyst is a metal or metal alloy, preferably a pyrophoric metal or a pyrophoric metal alloy on a carrier. The carrier is a silicate, preferably a layer silicate or framework silicate. As a metal Ag is in particular useful. Among the known fuels used are triaminoguanidine nitrate (TAGN), nitroguanidine (NIGU, NQ), 3-nitro-1,2,3-triazole-5-on and, in particular, diguanidine-5,5'-azotetrazolate (GZT).

The most important advantage of the gas-generating mixtures described in the two German patents mentioned above is according to the teaching in these patents the decrease in the burn-up temperature and the increase in the burn-up rate.

The gas-generating mixtures described in DE-C-44 01 213 and DE-C-44 01 214 do not contain low temperature melting and

high temperature melting slag formers and no slag traps according to the present invention. On the contrary, it is said that slag formers are not necessary.

Contrary to this allegation, the present inventors found that the use of low temperature melting and high temperature melting slag formers, in particular the use of the slag traps according to the present invention results in a significant reduction of toxic gaseous burn-up products. A part of the high temperature melting slag trap can be used as a carrier for a platinum metal and for a metal alloy consisting of platinum metals and, therefore, can function as a part of the catalyst.

In both of the above mentioned German patents the term "catalyst" is used in an extended sense and is an active part of the reaction, which "catalyst" can be reacted and acts to direct the reaction and/or to accelerate the reaction.

Therefore, it is not a catalyst in the strict sense of the word, since a catalyst is not a component to be reacted in a reaction. A catalyst in the strict sense of the word is not consumed during a reaction, i.e. is not reacted.

The definition of a catalyst further comprises that the catalyst is added to the reaction mixture only in a very low concentration. However, in both German patents the portion of the "catalyst" in that gas-generating mixture is up to 30% by weight and is therefore an essential part of the gas-generating mixture, also as regards its proportion in the mixture.

Thus, in summary, it is true that in DE-C-44 01 213 and DE-C-44 01 214 the term "catalyst" is used but the meaning of this

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term does not correspond to the common definition of a catalyst, as is also indicated in the two patents themselves.

The technical problem underlying the present invention vis-à-vis the prior art is to provide improved propellants for gas generators, in particular for airbags, the burn-up behaviour of which can be adjusted as desired and which minimize in particular the formation of toxic gases and of powder (dust-type) components which could exit from the housing of the gas generator and enter the lungs.

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The propelling charges for gas generators prepared from the propellants for gas generators are intended to be thermally stable, readily ignitable, fast-burning - even at low temperature, and well storable and ensure a high gas yield. In addition, said propellants for gas generators are intended to make it possible to reduce the size of the housing of the gas generator and the number of components and simplify the housing of the gas generator and consequently reduce its weight compared with known generators.

According to the present invention, these objects are achieved by a propellant for gas generators, comprising

(A) at least one fuel selected from the group comprising guanidine nitrate (GUNI; GuNO₃), dicyanamide, ammonium dicyanamide, sodium dicyanamide (Na-DCA), copper dicyanamide, tin dicyanamide, calcium dicyanamide (Ca-DCA), guanidine dicyanamide (GDCA), aminoguanidine bicarbonate (AGB), aminoguanidine nitrate (AGN), triaminoguanidine nitrate (TAGN), nitroguanidine (NIGU), dicyandiamide (DCD), azodicarbonamide (ADCA) as well as tetrazole (HTZ), 5-aminotetrazole (ATZ), 5-nitro-1,2,4-triazole-3-on (NTO), salts and mixtures thereof,

(B) at least one alkali metal nitrate or alkaline earth metal nitrate or ammonium nitrate, -chlorate or -perchlorate,

(C) at least one essentially chemically-inert slag trap which has a high fusion point selected from the group comprising Al_2O_3 , TiO_2 and ZrO_2 in highly dispersed form and mixtures thereof, and

optionally (D) at least one slag former selected from alkali metal and alkaline earth metal carbonates and -oxides, silicates, aluminates and aluminumsilicates, iron(III)oxide as well as silicon nitride (Si_3N_4), which results during burn-up in the formation of nitrogen (N_2) and silicon dioxide (SiO_2) for the further reaction and

optionally (E) at least one binder being soluble in water at room temperature.

Preferred fuels, component (A), are nitroguanidine (NIGU), 5-aminotetrazole (ATZ), dicyandiamide (DCD), dicyanamide, the salts thereof, in particular sodium- and calcium dicyanamide and guanidine nitrate, and mixtures thereof. These are virtually non-toxic, non-hygroscopic, sparingly soluble in water, thermally stable, burning even at low temperature and have a low impact and friction sensitivity. The gas yield during burn-up is high, wherein a large portion of nitrogen gas is developed.

Alkali metal salts (Li, Na, K) and alkaline earth metal salts (Mg, Ca, Sr, Ba) are examples for suitable salts of 5-aminotetrazole.

As oxidizing agents, component (B), alkali metal- or alkaline earth metal nitrates (such as lithium nitrate, sodium nitrate, potassium nitrate, magnesium nitrate, calcium nitrate,

strontium nitrate or barium nitrate), ammonium nitrate, alkali metal- or alkaline earth metal chlorates or perchlorates (such as lithium-, sodium-, potassium-, magnesium-, calcium-, strontium- or barium chlorate and lithium-, sodium-, potassium-, magnesium-, calcium-, strontium- or barium perchlorate) as well as ammonium perchlorate and mixtures thereof can be used. Potassium nitrate and strontium nitrate are preferred. Strontium nitrate is non-hygroscopic, non-toxic and allows a high gas yield during burn-up. Potassium nitrate, in addition, has a low burn-up temperature.

Examples for essentially chemically-inert slag traps which have a high fusion point, component (C), are Al_2O_3 , TiO_2 and ZrO_2 in highly dispersed form or mixtures thereof. Al_2O_3 having a BET-surface (according to DIN 66131) of $100 +/ - 15 \text{ m}^2/\text{g}$ (fusion point about $2,050^\circ\text{C}$), TiO_2 having a BET-surface of $50 +/ - 15 \text{ m}^2/\text{g}$ (fusion point about $1,850^\circ\text{C}$) and ZrO_2 having a BET-surface of $40 +/ - 10 \text{ m}^2/\text{g}$ (fusion point about $2,700^\circ\text{C}$) are particularly preferred. These highly dispersed oxides are commercially available for example under the trade names Aluminumoxid C, Titanoxid P25 and VP Zirkonoxid of Degussa AG. A4
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These pyrogenic oxides are obtained by the reaction of the respective metal chloride with H_2 and O_2 in the corresponding molar ratio by gas phase reaction (flame hydrolysis). These oxides have no pores and no defined agglomerates as is usually the case in the preparation by a wet process.

The term "slag trap", component (C), according to the present invention refers to an essentially chemically-inert metal oxide which has a high fusion point and is in highly dispersed form, i.e. these oxides have in comparison to oxides in conventional form a much higher surface.

For example, conventional Al_2O_3 as α -oxide has a BET-surface of only 5-10 m^2/g , conventional pigment- TiO_2 has a BET-surface of only 5-10 m^2/g and conventional ZrO_2 has a BET-surface of only 3-8 m^2/g (for fire-resistant products), whereas the metal oxides used in the propelling charges for gas generators according to the present invention have a BET-surface of about 40 up to about 100 m^2/g , particularly preferred of about 50 to about 100 m^2/g and, in particular, of about 100 m^2/g .

Furthermore, the slag traps according to the present invention are characterized by their high fusion point of about 1,850 to about 2,700°C. As a consequence of these high fusion points, the slag traps do not melt during the reaction and, thus, function as solids.

Furthermore, the slag traps according to the present invention are essentially chemically-inert compounds, i.e. the slag traps according to the present invention do not take part in chemical reactions during the burn-up reaction of the propelling charges for gas generators or do take part only to a small degree on the surface of the metal oxides used as a slag trap. The highly resolved lattices, i.e. the large inner surface of for example Al_2O_3 , TiO_2 or ZrO_2 (in highly dispersed form) cause on the one hand cooling of the burn-up products due to their inactivity and causes on the other hand take-up of, in particular, liquid and/or solid slag portions and particles, respectively, which are developed during burn-up. Thus, the tablet form of the propelling charges for gas generators remains during and after burn-up and possibly formed fragments and pieces can be easily filtered. That means, almost no dust is formed which could exit from the propelling charges for gas generators and consequently from the housing of the gas generators during burn-up. Thus, the

slag traps function as an internal filter in the propelling charges for gas generators themselves and, thus, substantially prevent the formation and exit of dust-type slag portions from the housing of the gas generator. Accordingly, an essential simplification of the filter of the housing of the gas generator is obtained, in that additional (mechanical) fine filters in the housing of the gas generator are in part not necessary. This also leads to an advantageous saving of weight of the airbag gas generator.

Simultaneously, the formation of dust-type particles which could exit the gas generator of an airbag and could enter the lungs is minimized by the formation of slags. Dust-type particles which can enter the lungs have a diameter of about 6 μm or less.

Optionally, slag formers, component (D), such as alkali metal and alkaline earth metal carbonates (e.g. sodium carbonate, potassium carbonate, magnesium carbonate, calcium carbonate, strontium carbonate and barium carbonate), alkali metal or alkaline earth metal oxides (e.g. sodium-, potassium-, magnesium-, calcium-, strontium- and barium oxide), silicates (e.g. hectorite), aluminates (e.g. sodium-beta-aluminate ($\text{Na}_2\text{O}_{11}\text{Al}_2\text{O}_3$) or tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$)) or aluminum silicates (e.g. bentonites or zeolites) or iron(III)oxide or mixtures thereof can be used.

The function of component (D) is to form an easily filterable slag during the burn-up of the propellant for gas generators.

In addition, the slag formers, component (D), can serve as a coolant. The silicates, aluminates and aluminum silicates react with the alkali metal and alkaline earth metal oxides which are formed during burn-up.

The present invention further relates to the use of catalysts on the basis of platinum metals (Ru, Os, Rh, Ir, Pd, Pt) or metal alloys of platinum metals or copper on highly dispersed slag traps as carriers in the solid propellants for gas generators of the present invention, in particular for use in solid propelling charges for gas generators for airbags.

A part of the slag trap, component (C), can serve as a carrier for a platinum metal or a metal alloy of platinum metals or copper in a catalytically effective layer thickness.

Platinum metals are ruthenium (Ru), osmium (Os), rhodium (Rh), iridium (Ir), palladium (Pd) and platinum (Pt). The catalysts used in the present invention are preferably based on Rh, Pd or Pt and, in particular, on Pt.

Examples for metal alloys of platinum metals are all catalytically effective metal alloys of the platinum metals mentioned above, preferably Pt/Pd and Pt/Rh alloys.

The metals or metal alloys of platinum metals are on the carrier in a catalytically effective layer thickness, preferably in a monolayer.

The catalysts are contained in the propelling charges for gas generators only in catalytic amounts. The weight portion with respect to component (C) is 0.1-5 % by weight, preferably 0.2-1.2 % by weight of component (C).

Preferred catalysts are those having Al_2O_3 as the highly dispersed carrier and Pt, Pd or Cu, in particular Pt, as metal.

Suitable catalysts are obtainable from Degussa AG, e.g. 1% Pt on gamma- Al_2O_3 or 1% Pd+Pt on gamma- Al_2O_3 .

The catalysts are useful to direct the reaction in that almost no toxic gaseous burn-up products such as carbon monoxide (CO), nitrogen oxides (NO_x) and ammonia (NH_3) are formed.

The above mentioned catalysts are in particular useful for the use in propelling charges for gas generators in airbags.

In addition to the advantages which result from the use of highly dispersed metal oxides (i.e. decrease of solid dust-type particles, i.e. of coarse and fine dust) the anyhow low portion of toxic gases is even more reduced.

The catalysts can be recycled by known processes from released, i.e. used airbags, as well as from non-released, i.e. airbags from used vehicles. This results in the reduction of waste which could pollute the environment and allows the re-use of the catalyst metals. The catalyst metal and metal alloy, respectively, is not oxidized during burn-up.

The catalyst must not be added as an additional part of the propelling charge for gas generators but the catalyst is part of a component (component (C)) being present anyhow in the propelling charge for gas generators.

Component (A) is present in an amount of about 20 to 60 wt-%, preferably from about 28 to 52 wt.-%, and in particular from about 45 to 51 wt.-%; component (B) is present in an amount of about 38 to about 63 wt.-%, preferably from about 38 to about 55 wt.-%, and in particular from about 39 to 45 wt.-%; component (C) is present in an amount from about 5 to 22 wt.-%, preferably from about 8 to 20 wt.-%, and in particular from about 9 to 11 wt.-%; finally, component (D), in case it is present at all, is present in an amount of about 2 to 12 wt.-%, preferably from about 4 to 10 wt.-%. All the wt.-%

given refer to the total composition of the propelling charge for gas generators.

Optionally, the propellant for gas generators may further contain a binder being soluble in water at room temperature as component (E). Preferred binders are cellulose compounds or polymers of one or more polymerizable olefinic unsaturated monomers. Examples of cellulose compounds are cellulose ethers, such as carboxymethylcellulose, methylcelluloseether, in particular methylhydroxyethylcellulose. A methylhydroxyethylcellulose which can be used satisfactorily is CULMINAL® MHEC 30000 PR supplied by the company Aqualon. Suitable polymers having binding action are polyvinylpyrrolidone, polyvinylacetate, polyvinylalcohol and polyvinylbutyral, for example Pioloform® B supplied by the company Wacker Chemie, Burghausen, Germany.

Further, metal salts of stearic acid being insoluble in water at room temperature, such as aluminum stearate, magnesium stearate, calcium stearate or zinc stearate, can be used as a binder (component (E)).

Furthermore, graphite is suitable as a binder.

Component (E) is present in an amount of 0 to 2 wt.-% and preferably from 0.3 to 0.8 wt.-%.

The binder, component (E), serves as desensitizing agent and as processing aid in the production of granular material or tablets (pellets) from the propellant for gas generators. It furthermore serves to reduce the hydrophilic nature of the propelling charges for gas generators and to stabilize them.

Working Example:

The preparation of the propellants for gas generators (Examples 1 to 57 of Table I) and of the propelling charges for gas generators was carried out as described in the following:

The roughly premixed raw materials (components (A), (B), (C) and optionally (D) and (E)) have been milled and predensified, respectively, by means of a ball mill.

The granulation of the propellant mixtures for gas generators has been carried out in a vertical mixer in that about 20 % of water has been added during steering and at an elevated temperature of about 40°C. After a short venting the obtained mixed mass has been grinded at room temperature through a grinding machine having a 1 mm-sieve. The thus obtained granulate has been dried for about two hours at 80°C in a drying oven. The ready-to-use granulate of the propellant for gas generators (grain-(size)distribution 0-1 mm) has been compressed into tablets (pellets) using a rotary pelleting machine. These pellets for the propelling charge for gas generators have been dried again at 80°C in a drying oven.

The tablets and pellets, respectively, used in the gas generators and prepared from the propellants for gas generators can be prepared according to processes known in the art, for example by hot press working, extruding, in rotary-pelleting (compression) machines or tabletting machines. The size of the pellets and tablets, respectively, depends on the desired burning time in each individual case.

The propellant for gas generators according to the present invention consists of non-toxic, inexpensive components which can be easily prepared and the processing of which is not problematic. The components which are more expensive, i.e.

the catalyst metal, can be recycled according to known procedures. Due to the thermal stability of the components a good storability is obtained. The mixtures are readily ignitable. They are fast-burning and ensure high gas yields with a very low proportion of CO, NO_x and NH₃ which proportion is below the admissible upper limit. Therefore, the mixtures according to the present invention are in particular suitable as gas-generating agents in the various airbag systems, as extinguishing agents or propellants.

The following examples 1 to 57 illustrate but do not limit the present invention. Examples 15, 18 and 21 are comparative examples in which conventional ZrO₂, TiO₂ and Al₂O₃ has been used.

Table I:

The superscripts of the table have the following meaning:

- 1 Titandioxid P25, supplied by Degussa AG
- 2 Zirkonoxid VP, supplied by Degussa AG
- 3 Aluminiumoxid C, supplied by Degussa AG
- 4 Titandioxid Kronos 3025, supplied by Kronos Titan-GmbH
- 5 Zirkonoxid, supplied by Merck
- 6 Aluminiumoxid NO 615-30 II 24, supplied by Nabaltec
- 7 Oxidation catalyst 1% Pt on Gamma-Aluminiumoxid, supplied by Degussa AG
- 8 Oxidation catalyst 1% Pd+Pt on Gamma-Aluminiumoxid, supplied by Degussa AG
- 9 Ironoxide, Bayoxide E8710, supplied by Bayer AG
- 10 Bentone EW, supplied by Rheox, Inc.
- 11 CULMINAL MHEC 30000 PR, supplied by Aqualon

Table I

Example No.		1	2	3	4	5	6
A = ATZ	[%]	30,2	32,8	29,75	29,7	29,75	29,7
NIGU	[%]	-	-	-	-	-	-
Ca-DCA	[%]	-	-	-	-	-	-
Na-DCA	[%]	-	-	-	-	-	-
TAGN	[%]	-	-	-	-	-	-
GuNO ₃	[%]	-	-	-	-	-	-
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B = KNO ₃	[%]	49,8	-	50,25	-	50,25	-
Sr(NO ₃) ₂	[%]	-	57,2	-	54,8	-	54,8
NaNO ₃	[%]	-	-	-	-	-	-
<hr/>							
C = TiO ₂ ¹	[%]	-	-	20,0	15,0	-	-
ZrO ₂ ²	[%]	-	-	-	-	20,0	15,0
Al ₂ O ₃ ³	[%]	10,0	10,0	-	-	-	-
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	-	-	-	-
<hr/>							
D = Iron(III)oxide ⁹	[%]	10,0	-	-	-	-	-
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	-	-
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E = Graphite	[%]	-	-	-	-	-	-
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-	-	-	-
Polyvinylbutyrate	[%]	-	-	-	0,5	-	0,5
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<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	17,8	19,3	17,6	21,7	17,6	18,0
Temperature (p=135*10 ⁵ Pa)	[K]	1780	2420	1780	2370	1780	2520
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<u>Measured Values</u> (in 60 dm ³ can):							
Carbonmonoxide	[ppm]	4000	2800	3000	3300	3000	3300
Nitrogenoxide	[ppm]	150	300	200	350	200	250
Ammonia	[ppm]	150	0	0	0	100	100
Coarse dust in the can	[g]	1,2	0,6	1,2	1,0	1,1	1,2
Fine dust in the can	[g]	0,2	0,1	0,3	0,3	0,3	0,3

Example No.		7	8	9	10	11	12
A = ATZ	[%]	29,75	32,8	29,75	32,8	21,5	25,6
NIGU	[%]	-	-	-	-	-	-
Ca-DCA	[%]	-	-	-	-	-	-
Na-DCA	[%]	-	-	-	-	-	-
TAGN	[%]	-	-	-	-	-	-
GuNO ₃	[%]	-	-	-	-	-	-
<hr/>							
B = KNO ₃	[%]	50,25	-	50,25	-	58,0	-
Sr(NO ₃) ₂	[%]	-	57,2	-	57,2	-	54,1
NaNO ₃	[%]	-	-	-	-	-	-
<hr/>							
C = TiO ₂ ¹	[%]	-	-	-	-	-	-
ZrO ₂ ²	[%]	-	-	-	-	-	-
Al ₂ O ₃ ³	[%]	10,0	-	10,0	-	10,0	10,0
Al ₂ O ₃ + 1%Pt ⁷	[%]	10,0	10,0	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	10,0	10,0	-	-
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D = Iron(III)oxide ⁹	[%]	-	-	-	-	-	5,0
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	10,0	5,0
<hr/>							
E = Graphite	[%]	-	-	-	-	0,5	-
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-	-	-	-
Polyvinylbutyrate	[%]	-	-	-	-	-	0,3
<hr/>							
<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	17,6	19,3	17,6	19,3	16,8	16,8
Temperature (p=135*10 ⁵ Pa)	[K]	1780	2420	1780	2420	2120	2420
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<u>Measured Values (in 60 dm³ can):</u>							
Carbonmonoxide	[ppm]	2500	2300	2300	2100	4500	4000
Nitrogenoxide	[ppm]	200	250	200	250	400	250
Ammonia	[ppm]	0	0	0	0	200	150
Coarse dust in the can	[g]	0,7	0,6	0,7	0,7	0,9	1,3
Fine dust in the can	[g]	0,2	0,2	0,2	0,1	0,3	0,5

Example No.		13	14	15	16	17	18
A = ATZ	[%]	-	-	-	-	-	-
NIGU	[%]	48,2	47,0	47,0	48,5	47,0	47,0
Ca-DCA	[%]	-	-	-	-	-	-
Na-DCA	[%]	-	-	-	-	-	-
TAGN	[%]	-	-	-	-	-	-
GuNO ₃	[%]	-	-	-	-	-	-
<hr/>							
B = KNO ₃	[%]	41,3	-	-	41,0	-	-
Sr(NO ₃) ₂	[%]	-	42,5	42,5	-	42,5	42,5
NaNO ₃	[%]	-	-	-	-	-	-
<hr/>							
C = TiO ₂ ^{1 or 4}	[%]	10,0 ¹	10,0 ¹	10,0 ⁴	-	-	-
ZrO ₂ ^{2 or 5}	[%]	-	-	-	10,0 ²	10,0 ²	10,0 ⁵
Al ₂ O ₃ ³	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	-	-	-	-
<hr/>							
D = Iron(III)oxide ⁹	[%]	-	-	-	-	-	-
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	-	-
<hr/>							
E = Graphite	[%]	-	0,5	0,5	-	0,5	0,5
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-	-	-	-
Polyvinylbutyrate	[%]	0,5	-	-	0,5	-	-
<hr/>							
<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	23,8	23,1	23,1	23,9	23,1	23,1
Temperature (p=135*10 ⁵ Pa)	[K]	2030	2490	2490	2080	2550	2550
<hr/>							
<u>Measured Values (in 60 dm³ can):</u>							
Carbonmonoxide	[ppm]	8000	6500	8000	6500	6500	8000
Nitrogenoxide	[ppm]	600	450	450	800	700	800
Ammonia	[ppm]	100	0	0	150	0	0
Coarse dust in the can	[g]	1,4	0,3	0,7	1,0	0,1	0,3
Fine dust in the can	[g]	0,6	0,4	0,3	0,3	0,3	0,3

Example No.		19	20	21	22	23	24
A = ATZ	[%]	-	-	-	-	-	-
NIGU	[%]	50,6	46,0	46,0	46,5	50,6	46,5
Ca-DCA	[%]	-	-	-	-	-	-
Na-DCA	[%]	-	-	-	-	-	-
TAGN	[%]	-	-	-	-	-	-
GuNO ₃	[%]	-	-	-	-	-	-
<hr/>							
B = KNO ₃	[%]	39,4	-	-	-	39,4	-
Sr(NO ₃) ₂	[%]	-	43,5	43,5	38,5	-	38,5
NaNO ₃	[%]	-	-	-	-	-	-
<hr/>							
C = TiO ₂ ¹	[%]	-	-	-	-	-	-
ZrO ₂ ²	[%]	-	-	-	-	-	-
Al ₂ O ₃ ^{3 or 6}	[%]	10,0 ³	10,0 ³	10,0 ⁶	15,0 ³	-	-
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	10,0	15,0
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	-	-	-	-
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D = Iron(III)oxide ⁹	[%]	-	-	-	-	-	-
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	-	-
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E = Graphite	[%]	-	0,5	0,5	-	-	-
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-	-	-	-
Polyvinylbutyrate	[%]	-	-	-	-	-	-
<hr/>							
<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	24,3	22,8	22,8	22,4	24,3	22,4
Temperature (p=135*10 ⁵ Pa)	[K]	2050	2380	2380	2330	2430	2330
<hr/>							
<u>Measured Values</u> (in 60 dm ³ can):							
Carbonmonoxide	[ppm]	5700	6000	8000	5000	4600	4200
Nitrogenoxide	[ppm]	300	450	600	300	200	250
Ammonia	[ppm]	0	0	0	0	0	0
Coarse dust in the can	[g]	1,0	0,7	0,8	0,3	1,2	0,5
Fine dust in the can	[g]	0,4	0,1	0,3	0,3	0,3	0,3

Example No.		25	26	27	28	29	30
A = ATZ	[%]	-	-	-	-	-	-
NIGU	[%]	50,6	46,5	43,5	37,4	48,0	-
Ca-DCA	[%]	-	-	-	-	-	-
Na-DCA	[%]	-	-	-	-	-	-
TAGN	[%]	-	-	-	-	-	-
GuNO ₃	[%]	-	-	-	-	-	51,7
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B = KNO ₃	[%]	39,4	-	45,9	-	41,4	-
Sr(NO ₃) ₂	[%]	-	38,5	-	52,1	-	37,8
NaNO ₃	[%]	-	-	-	-	-	-
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C = TiO ₂ ¹	[%]	-	-	-	-	-	-
ZrO ₂ ²	[%]	-	-	-	-	-	-
Al ₂ O ₃ ³	[%]	-	-	-	-	5,0	5,0
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	10,0	15,0	-	-	-	-
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D = Iron(III)oxide ⁹	[%]	-	-	5,0	-	5,0	5,0
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	5,0	10,0	-	-
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E = Graphite	[%]	-	-	0,6	0,5	0,6	-
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-	-	-	-
Polyvinylbutyrate	[%]	-	-	-	-	-	0,5
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<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	24,3	22,4	23,3	19,8	23,6	26,0
Temperature (p=135*10 ⁵ Pa)	[K]	2430	2330	2130	2820	1970	2100
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Measured Values (in 60 dm ³ can):							
Carbonmonoxide	[ppm]	4500	4000	6300	6700	8000	5500
Nitrogenoxide	[ppm]	250	250	400	450	150	900
Ammonia	[ppm]	0	0	0	0	250	10
Coarse dust in the can	[g]	1,1	0,4	1,3	1,3	1,5	0,6
Fine dust in the can	[g]	0,2	0,3	0,4	0,5	0,3	0,4

Example No.		31	32	33	34	35	36
A = ATZ	[%]	-	-	-	-	-	-
NIGU	[%]	-	43,0	17,7	9,0	18,1	16,0
Ca-DCA	[%]	27,8	3,0	17,7	23,8	-	-
Na-DCA	[%]	-	-	-	-	18,1	16,0
TAGN	[%]	-	-	-	-	-	-
GuNO ₃	[%]	-	-	-	-	-	-
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B = KNO ₃	[%]	-	-	-	57,2	-	58,0
Sr(NO ₃) ₂	[%]	62,2	45,5	54,6	-	53,8	-
NaNO ₃	[%]	-	-	-	-	-	-
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C = TiO ₂ ¹	[%]	-	-	-	-	-	-
ZrO ₂ ²	[%]	-	-	-	-	-	-
Al ₂ O ₃ ³	[%]	10,0	8,0	10,0	10,0	10,0	10,0
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	-	-	-	-
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D = Iron(III)oxide ⁹	[%]	-	-	-	-	-	-
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	-	-
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E = Graphite	[%]	-	-	-	-	-	-
Methylhydroxyethylcellulose ¹¹	[%]	-	0,5	-	-	-	-
Polyvinylbutyrate	[%]	-	-	-	-	-	-
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<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	11,4	22,5	15,8	14,0	17,4	14,7
Temperature (p=135*10 ⁵ Pa)	[K]	2440	2470	2420	1780	2230	1780
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<u>Measured Values</u> (in 60 dm ³ can):							
Carbonmonoxide	[ppm]	2800	8000	3600	8000	10000	450
Nitrogenoxide	[ppm]	700	1000	800	500	800	100
Ammonia.	[ppm]	0	0	0	50	3	2
Coarse dust in the can	[g]	2,2	0,6	1,2	3,2	1,3	1,5
Fine dust in the can	[g]	0,5	0,3	0,4	0,4	0,2	0,3

Example No.		37	38	39	40	41	42
A = ATZ	[%]	-	-	-	-	-	-
NIGU	[%]	-	-	-	-	-	-
Ca-DCA	[%]	26,0	28,7	-	-	-	-
Na-DCA	[%]	-	-	28,5	28,5	-	-
TAGN	[%]	-	-	-	-	48,6	22,7
GuNO ₃	[%]	-	-	-	-	-	22,7
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B = KNO ₃	[%]	-	61,3	-	61,0	41,4	34,6
Sr(NO ₃) ₂	[%]	59,6	-	61,5	-	-	-
NaNO ₃	[%]	-	-	-	-	-	-
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C = TiO ₂ ¹	[%]	14,0	10,0	10,0	10,0	-	-
ZrO ₂ ²	[%]	-	-	-	-	-	-
Al ₂ O ₃ ³	[%]	-	-	-	-	10,0	20,0
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	-	-	-	-
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D = Iron(III)oxide ⁹	[%]	-	-	-	-	-	-
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	-	-
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E = Graphite	[%]	-	-	-	-	-	-
Methylhydroxyethylcellulose ¹¹	[%]	0,4	-	-	-	-	-
Polyvinylbutyrate	[%]	-	-	-	0,5	-	-
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<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	10,9	11,7	9,7	10,7	26,2	23,4
Temperature (p=135*10 ⁵ Pa)	[K]	2400	1780	2240	1780	2140	1800
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<u>Measured Values</u> (in 60 dm ³ can):							
Carbonmonoxide	[ppm]	1500	1800	2000	2500	3000	2700
Nitrogenoxide	[ppm]	300	800	500	1000	150	350
Ammonia	[ppm]	10	5	15	3	160	24
Coarse dust in the can	[g]	1,0	1,7	1,1	1,5	1,4	0,8
Fine dust in the can	[g]	0,4	0,5	0,3	0,4	0,3	0,2

Example No.		43	44	45	46	47	48
A = ATZ	[%]	17,7	-	-	-	-	-
NIGU	[%]	-	-	-	-	-	-
Ca-DCA	[%]	-	-	18,8	-	-	-
Na-DCA	[%]	-	-	-	-	-	-
TAGN	[%]	17,7	-	-	-	-	-
GuNO ₃	[%]	-	54,2	18,8	50,0	50,0	51,5
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B = KNO ₃	[%]	44,6	35,8	52,4	-	-	-
Sr(NO ₃) ₂	[%]	-	-	-	39,4	39,4	38,0
NaNO ₃	[%]	-	-	-	-	-	-
<hr/>							
C = TiO ₂ ¹	[%]	-	-	-	-	10,0	-
ZrO ₂ ²	[%]	-	-	-	-	-	10,0
Al ₂ O ₃ ³	[%]	20,0	5,0	10,0	10,0	-	-
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	-	-	-	-
<hr/>							
D = Iron(III)oxide ⁹	[%]	-	5,0	-	-	-	-
Aluminumsilicate ¹⁰	[%]	-	-	-	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	-	-
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E = Graphite	[%]	-	-	-	0,6	0,6	-
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-	-	-	0,5
Polyvinylbutyrate	[%]	-	-	-	-	-	-
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<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	20,0	26,6	16,9	25,1	25,1	25,7
Temperature (p=135*10 ⁵ Pa)	[K]	1810	1780	1780	2120	2130	2170
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<u>Measured Values (in 60 dm³ can):</u>							
Carbonmonoxide	[ppm]	1000	5000	7000	6000	4000	3500
Nitrogenoxide	[ppm]	150	400	150	800	100	500
Ammonia	[ppm]	50	100	150	5	0	10
Coarse dust in the can	[g]	1,0	2,0	1,8	1,5	1,0	0,5
Fine dust in the can	[g]	0,4	0,5	0,6	0,4	0,5	0,3

Example No.		49	50	51	52	53	54
A = ATZ	[%]	29,75	30,2	30,2	26,5	26,8	33,7
NIGU	[%]	-	-	-	8,0	-	-
Ca-DCA	[%]	-	-	-	-	-	-
Na-DCA	[%]	-	-	-	-	-	-
TAGN	[%]	-	-	-	-	-	-
GuNO ₃	[%]	-	-	-	-	8,0	-
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B = KNO ₃	[%]	50,25	49,8	49,8	32,5	32,2	56,3
Sr(NO ₃) ₂	[%]	-	-	-	-	-	-
NaNO ₃	[%]	-	-	-	15,0	15,0	-
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C = TiO ₂ ¹	[%]	-	-	-	-	-	10,0
ZrO ₂ ²	[%]	3,0	10,0	-	-	-	-
Al ₂ O ₃ ³	[%]	14,0	10,0	10,0	18,0	18,0	-
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-	-	-	-
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	3,0	-	-	-	-	-
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D = Iron(III)oxide ⁹	[%]	-	-	-	-	-	-
Aluminumsilicate ¹⁰	[%]	-	-	10,0	-	-	-
Siliconnitride Si ₃ N ₄	[%]	-	-	-	-	-	-
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E = Graphite	[%]	-	-	-	-	-	-
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-	-	-	-
Polyvinylbutyrate	[%]	-	-	-	-	-	-
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<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	17,6	17,8	19,3	19,4	19,7	19,8
Temperature (p=135*10 ⁵ Pa)	[K]	1780	1780	1920	1800	1780	1820
<u>Measured Values</u> (in 60 dm ³ can):							
Carbonmonoxide	[ppm]	2600	3000	4500	3500	6500	8000
Nitrogenoxide	[ppm]	300	200	300	800	500	250
Ammonia	[ppm]	23	50	50	0	5	300
Coarse dust in the can	[g]	1,0	1,1	1,2	0,8	1,0	0,8
Fine dust in the can	[g]	0,2	0,4	0,5	0,2	0,2	0,3

Example No.		55	56	57			
A = ATZ	[%]	30,35	31,66	29,75			
NIGU	[%]	-	-	-			
Ca-DCA	[%]	-	-	-			
Na-DCA	[%]	-	-	-			
TAGN	[%]	-	-	-			
GuNO ₃	[%]	-	-	-			
B = KNO ₃	[%]	49,65	-	50,25			
Sr(NO ₃) ₂	[%]	-	56,34	-			
NaNO ₃	[%]	-	-	-			
C = TiO ₂ ¹	[%]	-	-	-			
ZrO ₂ ²	[%]	-	-	-			
Al ₂ O ₃ ³	[%]	10,0	9,0	20,0			
Al ₂ O ₃ + 1%Pt ⁷	[%]	-	-	-			
Al ₂ O ₃ + 1%(Pd+Pt) ⁸	[%]	-	-	-			
D = Iron(III)oxide ⁹	[%]	6,0	-	-			
Aluminumsilicate ¹⁰	[%]	4,0	3,0	-			
Siliconnitride Si ₃ N ₄	[%]	-	-	-			
E = Graphite	[%]	-	-	-			
Methylhydroxyethylcellulose ¹¹	[%]	-	-	-			
Polyvinylbutyrate	[%]	-	-	-			
<u>Calculated Values:</u>							
Gas yield (V=constant)	[mol/kg]	18,2	18,8	17,6			
Temperature (p=135*10 ⁵ Pa)	[K]	1780	2390	1780			
<u>Measured Values (in 60 dm³ can):</u>							
Carbonmonoxide	[ppm]	6000	7500	3500			
Nitrogenoxide	[ppm]	100	250	400			
Ammonia	[ppm]	150	0	0			
Coarse dust in the can	[g]	1,5	0,7	0,7			
Fine dust in the can	[g]	0,4	0,3	0,3			

The burn-up tests have been carried out in a practise-orientated housing of a gas generator for a 60 litre driver-airbag having the original size, igniter and filter package of stainless steel.

The weight of the propelling charge for gas generators was 50 to 55 g, depending on the gas yield of the individual composition of the propellant for gas generators.

Depending on the burn-up properties the pellets had a diameter of 4 to 6 mm and a height of 1.5 and 2.1 mm, respectively.

The gas yield and the temperature lie in a range which is advantageous for propellants for gas generators for airbags.

The terms "coarse dust" and "fine dust" in the table refer to the dust in the can after burn-up.

The values measured for CO, NO_x and NH₃ given in the table relate to a 60 litre can. The obtained values are good taking into consideration that a non-optimised test gas generator has been used.

From the comparison of Examples 14 and 15, 17 and 18, and 20 and 21, the effect obtained by the use of highly dispersed oxides in comparison to the conventional oxides is illustrated. The decrease in particle ejection (coarse and fine dust) for the system nitroguanidine/strontium nitrate has been about 20 to 40% due to the specific highly dispersed slag trap (C) used according to the present invention in comparison to the conventional oxides of the same chemical structural formula but having a lower specific surface. In addition, the reduction of toxic gases of about 10 to 25% due to the improvement of the burn-up by use of the specific slag

traps (C) used according to the present invention and the properties thereof is evident.

Furthermore, the additional beneficial effect of highly dispersed slag traps (C), having catalysts on the surface, with respect to the formation of toxic gases can be seen from the comparison of the propellants for gas generators according to e.g. Examples 2 to 8 and 10.

The portions of CO and NO_x are according to Examples 8 and 10 (with catalyst) below those of Example 2 (without catalyst, however, apart from that having the same composition).

Particularly preferred compositions are those of Examples 14, 17 and 20.

The thermodynamical data of the various compositions have been calculated with respect to the oxygen-balance-excess for which the smallest possible amount of toxic gases during burn-up has been expected.